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(71) Applicant
Chevron Research Company (USA–Delaware),
525 Market Street, San Francisco, California 94105,
United States of America

(72) Inventor
William A Sweeney

(74) Agent and/or Address for Service
Haseltine Lake & Co,
Hazlitt House, 28 Southampton Buildings, Chancery Lane, London WC2A 1AT

(54) Stable emulsifier for substituted succinic anhydride compositions

(57) A stable polyethyleneoxy-containing emulsifier particularly suitable for use in forming stable hydrocarbyl-substituted succinic anhydride/emulsifier compositions is represented by the general formula:

$$R{-}W{-}[{-}Y{-}(COOH)_m]_n$$

wherein R is a hydrophobic alkyl, alkylaryl, arylalkyl or acyl group containing from 8 to 30 carbon atoms;

W is a water-soluble polyethyleneoxy-containing group having from 3 to 80 ethylene oxide units which is independently connected to R and Y through oxygen, sulfur, or nitrogen linkages;

$-[-Y-(COOH)_m]_n$ is a capping group for the oxygen, sulfur or nitrogen linkages on W not connected to R, wherein Y contains from 1 to 9 carbon atoms, provided that no more than 7 carbon atoms are methylene carbons;

m is 1 or 2;

n is 1/3, 1/2, 1, 2, or 3;

and the hydrophile-lipophile balance is between 9 and 18 on the HLB scale.

Aqeuous emulsions of these compositions can be used to impart water repellency to surfaces containing groups reactive to anhydrides and also in the production of sized paper.

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SPECIFICATION

Stable emulsifier for substituted succinic anhydride compositions

This invention relates to a stable polyethyleneoxy-containing emulsifier and an improved hydrocarbyl-substituted succinic anhydride/emulsifier composition. This invention also relates to an improved method for imparting water repellency to surfaces containing groups reactive to anhydrides. A further aspect of this invention relates to an improved method for the sizing of paper and paperboard products.

It is well known in the art that hydrocarbyl-substituted succinic anhydrides are good for treating paper, fabric, or other surfaces to impart water repellency. As indicated in U.S. Patent Nos. 3,102,064, 3,821,069, 3,968,005, and 4,040,900 (RE 29,960), these compositions are particularly useful for sizing paper.

It is also known that these succinic anhydrides are best applied for such purposes in a highly dispersed form, such as aqueous emulsion. See, for example, U.S. Patent No. 4,040,900 (RE 29,960), which describes paper sizing emulsions made from mixtures comprising a substituted cyclic dicarboxylic acid anhydride and polyoxyalkylene alkyl or alkylaryl ether or the corresponding mono- or di-ester.

Long-chain diester emulsifiers, as well as monoesters, alkyl phenol ethoxylates and alcohol ethoxylates, are disclosed in U.S. Patent No. 4,040,900 (RE 29,960) as useful emulsifiers for substituted succinic anhydrides.

A major drawback of these prior art emulsifiers is the fact that, once formed, the succinic anhydride-emulsifier mixtures are unstable and must be promptly used. There therefore exists a need in the art for substituted succinic anhydride-emulsifier mixtures which demonstrate enhanced stability upon aging or storage.

The present invention provides a novel emulsifier of the general formula:

$$R-W-[-Y-(COOH)_m]_n$$

wherein R is a hydrophobic alkyl, alkylaryl, aryl-alkyl or acyl group containing from 8 to 30 carbon atoms;

W is a water-soluble polyethyleneoxy-containing group having from 3 to 80 ethylene oxide units which is independently connected to R and Y through oxygen, sulfur or nitrogen linkages;

$-[-Y-(COOH)_m]_n$ is a capping group for the oxygen, sulfur or nitrogen linkages on W not connected to R, wherein Y contains from 1 to 9 carbon atoms, provided that no more than 7 carbon atoms are methylene carbons;

m is 1 or 2;

n is 1/3, 1/2, 1, 2, or 3;

and the hydrophile-lipophile balance (HLB) is between 9 and 18.

The present invention additionally provides a stable hydrocarbyl-substituted succinic anhydride/emulsifier composition comprising:

(A) 70 to 99.5% of a normally liquid hydrocarbyl-substituted succinic anhydride containing from 6 to 50 carbon atoms in the substituent; and

(B) 0.5 to 30% of the emulsifier defined above.

The present invention further provides a method of imparting water repellency to surfaces containing groups reactive to anhydrides which comprises impregnating said surfaces with an aqueous emulsion of the substituted succinic anhydride/emulsifier composition of the invention.

The present invention is also concerned with a method of sizing paper which comprises intimately dispersing within the wet pulp, prior to the ultimate conversion of said pulp into a dry web, an aqueous emulsion of the substituted succinic anhydride/emulsifier composition of the invention.

It has been found, in accordance with the invention, that certain derivatives of polyethyleneoxy-containing (or "polyethylene glycol-based") emulsifiers, wherein the free hydroxyl groups are capped with small carbon-containing groups, are surprisingly effective emulsifiers upon aging in substituted succinic anhydride. These emulsifiers provide stable mixtures with substituted succinic anhydride and do not react with the anhydride under storage conditions.

Advantageously, the substituted succinic anhydride-emulsifier mixtures of the present invention are highly effective in treating various surfaces to impart water-repellency. These compositions are particularly useful as superior paper sizing agents.

The hydrocarbyl-substituted succinic anhydride useful for preparing the anhydride/emulsifier composition of the present invention is a hydrophobic molecule. Usually it will have one substituent in the 3-position, but it may have been substituents in both the 3- and 4-positions. In general, the substituent will be an alkyl, alkenyl or aralkyl group. Other elements may be present in a minor amount, such as a sulfur or other linkage. The total number of carbon atoms in the substituent is between 6 and 50. A preferred substituent size is between 10 and 30.

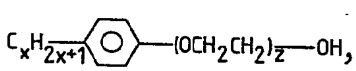
More preferred is between 12 and 25. A preferred embodiment of the contemplated anhydrides is the alkenyl succinic anhydride made by allowing an olefin to react with maleic anhydride by the well-known "Ene" reaction. Also suitable is the "Diels-Alder" product derived from maleic anhydride and a conjugated diene. For the present purposes, we shall refer to the anhydrides contemplated as "ASA".

The emulsifier of the present invention possesses three essential properties. First, it is soluble in ASA at ambient temperatures. Secondly, it is stable to storage when dissolved in ASA. Thirdly, it has surfactant power to emulsify ASA in water. To satisfy these requirements, the present emulsifier contains no free –SH, –OH or –NH groups which could react with ASA and it has a hydrophile-lipophile balance (HLB) between 9 and 18.

Generally, to achieve the desired HLB, the emulsifiers will contain between 3 and 80 average moles of ethylene oxide, depending on the size of the lipophilic and other hydrophilic groups present. More commonly, the suitable range of moles of ethylene oxide employed will be from 5 to 40.

The present emulsifier can be prepared from commercially available polyethylene glycol-derived emulsifiers which contain free hydroxyl groups. These commercially available emulsifiers are themselves soluble in ASA and are effective for emulsifying the anhydride in water. However, they are not stable in ASA on storage due to the presence of the hydroxyl groups. Examples of this class of hydroxyl-containing compounds are described in U.S. Patent No. 4,040,900 (RE 29,960) and include the polyethylene glycol derivatives of long-chain alcohols, alkylphenols and carboxylic acids, which are commonly used to emulsify oils in water. In general, these compounds will contain one free hydroxyl group and can be represented by the following formulae:

$$C_xH_{2x+1}\overset{O}{\overset{\|}{C}}-(OCH_2CH_2)_z-OH,$$



$$C_xH_{2x+1}(OCH_2CH_2)_z-OH,$$

wherein x is an integer from 8 to 24 and z is an integer from 5 to 20. Typical commercial examples of these hydroxyl-containing emulsifiers include Igepal CO-630 (GAF), Triton X-100 (Rohm and Hass), Tergitol TMN-6 and Tergitol 15-S-9 (Union Carbide), and PEG 400 mono and dilaurate (Stepan).

In addition to the above monohydroxy-containing surfactants, suitable surfactants may contain various hydrophilic moieties familiar to the art. In addition to polyethyleneoxy groups, they may contain glyceryl, polyglyceryl, anhydrosorbityl or pentaerythrityl groups, and the like. With these compounds more than one hydroxyl group is present which must be capped to form the surfactants of the present invention. Small amounts of propyleneoxy groups may also be present. It is not desirable to employ surfactants which possess more than about four hydroxyl groups because of the excessive amount of capping required.

Also contemplated are surfactants in which sulfur or nitrogen linkages are involved, between the hydrophilic group and either the hydrophobic or the capping group. For example, ethoxylated mercaptans or ethoxylated fatty acid amides can be used. Ethoxylated sulfonamides can also be used.

The hydrophobic moiety may be straight chain, branched or cyclic. It may be alkyl, alkylaryl or aryl-alkyl. It may also include an acyl attachment.

The above-described compounds are converted to the emulsifiers of the present invention by reacting the free hydroxyls with a small carbon-containing reagent which adds a free carboxyl at the same time as it caps, or covers up, the hydroxyls. Generally, the capping group will have only a minor effect on the hydrophile-lipophile balance (HLB) of the emulsifier because the free carboxyl group counteracts the effect of the cap on the HLB. One must select the surfactant and capping group to ensure that the capped emulsifier is within the desired HLB range. Enough capping reagent is used to cover up all the reactive –SH, –OH and –NH groups in the surfactant employed.

Suitable capping reagents either contain a free carboxyl group which does not react during the capping reaction or contain a nascent carboxyl which is formed during the capping reaction, or both. An example of the former type is chloroacetic acid which, after reaction, leaves a carboxymethyl capping group. An example of the latter type is succinic anhydride which, after

reaction, leaves a carboxypropionyl capping group.

The carboxymethyl type of cap can be added by a process similar to that described in U.S. Patent No. 2,623,900. This is suitable for making emulsifiers of the present invention but suffers from the disadvantage of forming a sodium chloride byproduct. This capping reaction produces an ether linkage to the hydrophilic moiety of the emulsifier. Other stable linkages are also contemplated. For example, an ester linkage could be formed by reaction of the monoacyl chloride of a polycarboxylic acid.

Preferred capping reagents are those that form a carboxyl derivative linkage, such as ester, amide, and the like, to the hydrophilic moiety.

While the capping reagents are normally monofunctional, they can also be difunctional or even trifunctional, as long as the structural requirements are met proportionately for each functional group.

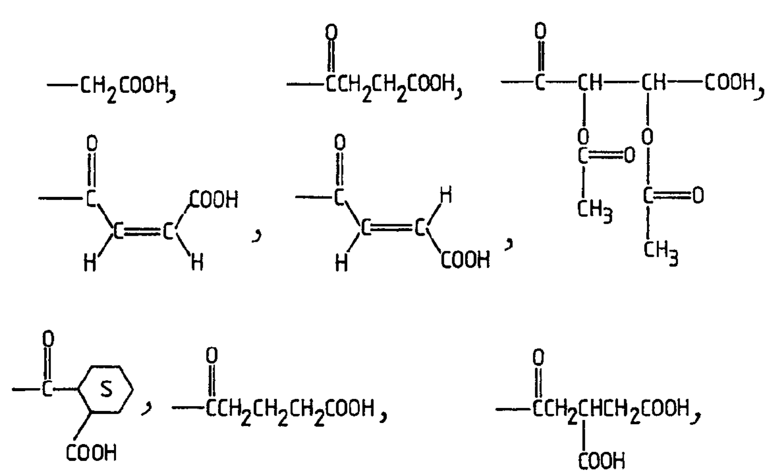
The cyclic anhydride capping reagents are particularly preferred because they require no catalyst or coreactant and no byproducts are formed. Consequently, no additional processing steps are required. Examples of suitable cyclic anhydrides include maleic, succinic, glutaric, itaconic, citraconic, glutaconic, diglycolic, thiodiglycolic, and the like. Anhydrides from acetyl malic acid or diacetyl tartaric acid are suitable. Bicyclic anhydrides, such as tetrahydrophthalic and hexahydrophthalic, are suitable. The adduct of maleic anhydride with cyclopentadiene is suitable. Dianhydrides such as pyromellitic dianhydride and benzophenone tetracarboxylic dianhydride are suitable. In this case, both anhydride groups each react with a separate hydroxyl group, so only half the molecule is considered one capping group.

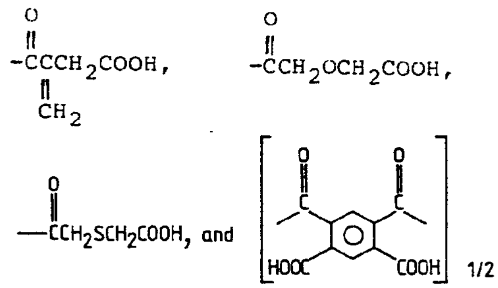
The cyclic anhydride may also contain a pendant carboxyl group before reaction, as in tricarballylic anhydride, aconitic anhydride or acetyl citric anhydride. In this case, the derived emulsifier of the present invention contains two pendant carboxyl groups for each capping reagent.

In the capping group on the emulsifier, designated $-[-Y-(COOH)_m]_n$ in the formula above, Y will generally contain from 1 to 9 carbon atoms, provided that no more than 7 carbon atoms are methylene carbon atoms. By "methylene" I mean any carbon atom which has at least three bonds attached to hydrogen or to another carbon atom. Therefore, methyl and some methine groups are included in this definition. The capping group should have relatively few methylene carbon atoms, which are lipophilic, so that the hydrophile-lipophile balance (HLB) of the emulsifier is not significantly altered. Carbon atoms taking part in carbon-carbon double bonds are also counted, but as equal to 2/3 of a methylene carbon. Preferably, Y will contain from 1 to 4 carbon atoms. The capping groups derived from the cyclic anhydrides will contain from 4 to 10 carbon atoms per anhydride group, including the pendant carboxyl produced. The smallest cyclic anhydrides contemplated, such as maleic and succinic anhydride, contain 4 carbon atoms. Up to 6 additional carbon atoms may be present, either in the anhydride ring or attached to it. With a dianhydride capping reagent, these numbers may be doubled. Inert groups, such as an ether or thio linkage, may also be present in the cyclic anhydride. For example, diglycolic and thiodiglycolic anhydride are suitable capping reagents. The smaller cyclic anhydrides containing four or five carbon atoms are preferred.

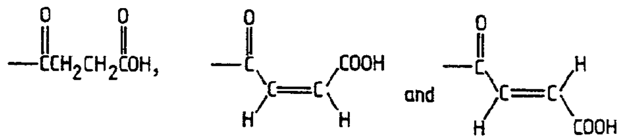
If the capping group contains a reactive function such as the double bond in a maleyl monoester, reactions known to the art may be performed with this function as long as the product conforms to the composition of this invention. For example, isomerization of a maleyl monoester to a fumaryl monoester yields a suitable emulsifier.

Examples of suitable capping groups on the emulsifier of the invention include the following:





Preferred capping groups include:



The hydrophobic/hydrophilic balance of the capped emulsifiers is in the normal emulsifier-detergent range. One way of defining this balance is by the use of the HLB scale (Hydrophile-Lipophile Balance). See P. Becker, Chapter 18, in "Nonionic Surfactants", M. J. Schick, Editor, Marcel Dekker (1967). The hydrophile-lipophile balance is an indication of the size and strength of the hydrophilic (water-loving or polar) groups, and the lipophilic (oil-loving or non-polar) groups in a surfactant material expressed by a numerical value designated the HLB number. On that scale, for my oil-in-water capped emulsifiers, the HLB should be about 9 to 18, preferably 11 to 16.

The HLB may be estimated by comparison of various properties, such as water solubility, with emulsifiers of known HLB. Alternatively, the HLB may be calculated by several procedures known to the art. See, for example, J. T. Davies, Second Proceedings International Congress on Surface Activity, page 426 (1957). A simple approach with polyethyleneoxy-containing nonionic compounds is to divide the weight percent polyethyleneoxide by five. We have estimated the HLB this way for several emulsifiers of the present invention by including the weight percent of the pendant carboxyl with the polyethyleneoxide. Very good ASA emulsions in water are obtained when the estimated HLB is in the 11 to 16 range.

The emulsifier of the present invention is prepared by reacting the unstable hydroxyl-containing emulsifier described above with the capping reagent until the hydroxyl groups have reacted. Generally, from a few minutes to several hours are required for this reaction at temperatures from about 80°C to 200°C. With esterification catalysts, lower temperatures and shorter times may be employed. Before making the ASA/emulsifier composition of the present invention, it is preferable to remove any byproducts which may have been formed, such as sodium chloride or hydrogen chloride. The capped emulsifier is then blended into the ASA, yielding the ASA/emulsifier composition of the invention.

Alternatively, when the capping reagent is sufficiently reactive, the hydroxyl-containing emulsifier may be first dissolved in the ASA and then reacted with the capping reagent.

In addition to the ability to provide stable self-emulsifying mixtures with ASA, the emulsifiers of the present invention possess unusual surfactant properties. The pendant carboxyl groups can ionize at high pH and can form complexes with metal ions.

The ASA/emulsifier compositions of the present invention comprise 70 to 99.5 parts by weight, preferably 80 to 98 parts, of the substituted succinic anhydride and 0.5 to 30 parts by weight, preferably 2 to 20 parts, of the capped emulsifier. These ASA/emulsifier combinations are easy to make at a central location and can be stored and shipped to the location where the ASA emulsions will be made. The two components are miscible and the mixture is liquid at ambient temperatures.

This ASA/emulsifier composition readily emulsifies into water of various hardness and pH with simple mixing in the absence of high shear. Fine droplets are formed and the emulsion is stable until it is used for treating a surface which contains groups reactive to the anhydride. The time between formation and use could range from a few seconds to several hours. Longer times are generally not preferred because the anhydride groups will gradually be hydrolyzed by the water present.

The water used can be relatively pure or can contain the usual impurities in domestic water. It can have a pH above or below 7, generally in the range of 3 to 11. Calcium and magnesium hardness ions may be present.

The amount of ASA suspended in the water can vary widely, from a few parts per million to 10% or more depending on the use and method of application. For wood or fabric treatment, concentrations around 1% may be used, whereas for internal paper sizing, the concentration in

the pump slurry is normally below about 100 parts per million. Thereby about 0.1 to 1% of ASA is finally absorbed on the paper.

Surfaces to be treated with the ASA/emulsifier compositions of the invention to gain water repellency will contain integral groups which are reactive to the ASA anhydride group. This normally will involve reaction with groups such as hydroxyl, amino or mercapto. A preferred type of material which may be treated with emulsions of the compositions of the invention contains carbohydrate molecules, such as cellulose or starch, at the surface of the material. These materials contain many hydroxyl groups which can react with the ASA.

As stated above, the ASA/emulsifier compositions of the present invention may be used to impart water repellency to cellulosic materials. The water-repellent compositions described above are preferably applied to the material in aqueous emulsions. The emulsion may be sprayed onto the material or the material may be dipped into the emulsion in order to distribute the derivative evenly throughout the material. The impregnated material is then withdrawn from the solution and air dried. After air drying, the material is then heated, preferably to a temperature in excess of 100°C, to effect a curing of the impregnated agent within the material. It has been found that one may conveniently use a temperature of about 125°C for a period of 15 to 20 minutes. At lower temperatures, longer periods of time are required to effect the curing process. Lower temperatures and shorter times may be used if an acylation catalyst is present. To be commercially practical, the curing time should be as short as possible and generally less than one hour. At higher temperatures, the heat curing may be accomplished in shorter periods of time. The upper limit of temperature at which the heat curing process may be carried out is limited to the temperatures at which the cellulosic material begins to decompose. Using the composition of the present invention, it is preferred to impregnate the material with from about 0.5 to 3% by weight of the material of the ASA/emulsifier composition.

The ASA/emulsifier compositions of the present invention may additionally be used as paper sizing agents. These novel sizing agents display all of the features and advantages of prior art sizing agents. Moreover, the novel sizing agents of this invention impart to paper sized therewith a particularly good resistance to acidic liquids such as acid inks, citric acid, lactic acid etc. as compared to paper sized with the sizing agents of the prior art. In addition to the properties already mentioned, these sizing agents may also be used in combination with alum as well as with any of the pigments, fillers and other ingredients which may be added to paper. The sizing agents of the present invention may also be used in conjunction with other sizing agents so as to obtain additive sizing effects. A still further advantage is that they do not detract from the strength of the paper and when used with certain adjuncts will, in fact, increase the strength of the finished sheets. Only mild drying or curing conditions are required to develop full sizing value.

The actual use of these sizing agents in the manufacture of paper is subject to a number of variations in technique, any of which may be further modified in light of the specific requirements of the practitioner. It is important to emphasize, however, that with all of these procedures, it is most essential to achieve a uniform dispersal of the sizing agent throughout the fiber slurry, in the form of minute droplets which can come in intimate contact with the fiber surface. Uniform dispersal may be obtained by adding the sizing agent to the pulp or by adding a previously formed, full dispersed emulsion. Chemical dispersing agents may also be added to the fiber slurry.

Another important factor in the effective utilization of the sizing agents of this invention involves their use in conjunction with a material which is either cationic in nature or is, on the other hand, capable of ionizing or dissociating in such a manner as to produce one or more cations or other positively charged moieties. These cationic agents, as they will be hereinafter referred to, have been found useful as a means for aiding in the retention of sizing agents herein as well as for bringing the latter into close proximity to the pulp fibers. Among the materials which may be employed as cationic agents in the sizing process, one may list alum, aluminum chloride, long chain fatty amines, sodium aluminate, substituted polyacrylamide, chromic sulfate, animal glue, cationic thermosetting resins and polyamide polymers. Of particular interest for use as cationic agents are various cationic starch derivatives including primary, secondary, tertiary or quaternary amine starch derivatives and other cationic nitrogen substituted starch derivatives, as well as cationic sulfonium and phosphonium starch derivatives. Such derivatives may be prepared from all types of starches including corn, tapioca, potato, waxy maize, wheat and rice. Moreover, they may be in their original granule form or they may be converted to pregelatinized, cold water soluble products.

Any of the above noted cationic agents may be added to the stock, i.e., the pulp slurry, either prior to, along with, or after the addition of the sizing agent. However, in order to achieve maximum distribution. It is preferable that the cationic agent be added either subsequent to or in direct combination with the sizing agent. The actual addition to the stock of either the cationic agent or the sizing agent may take place at any point in the paper making process prior to the ultimate conversion of the wet pulp into a dry web or sheet. Thus, for example, these sizing

agents may be added to the pulp while the latter is in the headbox, beater, hydropulper or stock chest.

Further improvements in the water resistance of the paper prepared with these novel sizing agents may be obtained by curing the resulting webs, sheets, or molded products. This curing process involves heating the paper at temperatures in the range of from 80° to 150°C for periods of from 1 to 60 minutes. However, it should again be noted that post curing is not essential to the successful operation of this invention.

The sizing agents of this invention may, of course, be successfully utilized for the sizing of paper prepared from all types of both cellulosic and combinations of cellulosic with non-cellulosic fibers. The cellulosic fibers which may be used include bleached and unbleached sulfate (kraft), bleached and unbleached sulfite, bleached and unbleached soda, neutral sulfite, semi-chemical chemiground-wood, ground wood, and any combination of these fibers. These designations refer to wood pulp fibers which have been prepared by means of a variety of processes which are used in the pulp and paper industry. In addition, synthetic fibers of the viscose rayon or regenerated cellulose type can also be used.

All types of pigments and fillers may be added to the paper which is to be sized with the novel sizing agents of this invention. Such materials include clay, talc, titanium dioxide, calcium carbonate, calcium sulfate, and diatomaceous earths. Other additives, including alum, as well as other sizing agents, can also be used with these sizing agents.

With respect to proportions, the sizing agents may be employed in amounts ranging from about 0.05 to about 3.0% of the dry weight of the pulp in the finished sheet or web. While amounts in excess of 3% may be used, the benefits of increased sizing properties are usually not economically justified. Within the mentioned range the precise amount of size which is to be used will depend for the most part upon the type of pulp which is being utilized, the specific operating conditions, as well as the particular end use for which the paper is destined. Thus, for example, paper which will require good water resistance or ink holdout will necessitate the use of a higher concentration of sizing agent then paper which does not.

The following examples are provided to illustrate the invention.

EXAMPLES

Example 1

The alkenyl succinic anhydride (ASA) employed in this example was a commercial type of liquid C_{15-20} ASA prepared by the "Ene" reaction of maleic anhydride with C_{15-20} olefins. The olefins consisted of a 50/50 mixture of straight chain internal olefins and branched chain propylene oligomer, both of which covered the C_{15}–C_{20} range, inclusive.

A 10% solution of Igepal CO-630, a commercial nonionic oil-in-water emulsifier, was made in the above ASA. This was a clear homogeneous solution at room temperature. One drop (0.026 g) of this mixture was shaken with 25 ml of water for 15 seconds in a stoppered graduate. A stable white emulsion was formed. This emulsifier, which has an HLB of 13.0, is therefore an excellent emulsifier for ASA when freshly mixed.

The 10% emulsifier in ASA mixture was allowed to stand at room temperature. After one week it would no longer form a stable emulsion. Similarly, when aging was accelerated by heating for 3 hours at 80°C, the mixture would not form a stable emulsion.

Similar results were obtained with five other commercial emulsifiers, namely, Tergitol TMN-6, Tergitol 15-S-12, Triton X-114, Triton X-100 and Igepal CO-620. After heating for three hours at 80°C, the 10% mixtures in ASA had lost their self-emulsifying power. The HLB of these emulsifiers ranged from 11.7 to 14.5.

This example shows that commercial emulsifiers, which form excellent emulsions when freshly mixed with ASA, do not from stable emulsions with ASA after aging the mixture.

Example 2

Igepal CO-630 was mixed in a 1/1 mole ratio with succinic anhydride and heated at 80°C for four hours. During that time the solid succinic anhydride all dissolved. An infrared analysis of the product indicated that a monoester had formed. An intense ester carbonyl absorption at 1735 cm^{-1} and carboxyl absorption at 3150 cm^{-1} was present. The hydroxyl absorption at 3480 cm^{-1} of the alkylphenol ethoxylate had disappeared.

The HLB of this capped emulsifier is estimated at 12.5.

Example 3

The capped emulsifier of Example 2 was mixed into the ASA of Example 1 at the 10% level. A homogeneous solution at room temperature was obtained.

When this mixture was tested for emulsifying power by the procedure described in Example 1, it formed an excellent emulsion in water. However, in this case, the mixture was stable to storage. After accelerated aging, 3 hours at 80°C, it still gave an excellent emulsion.

Therefore, the novel emulsifier of Example 2 exemplifies the present invention. It can be used

to make ASA/emulsifier compositions which are stable to storage.

Example 4

Igepal CO-630 was capped with a series of different anhydride reagents as in Example 2 and the reaction products were tested as emulsifiers for ASA using the procedures described in Example 1. The results are listed in Table I.

TABLE I

Emulsifiers made from Igepal CO-630 and Various Cyclic Anhydrides

Cyclic Anhydride	Product HLB	ASA Emulsion Rating[1] Fresh	Aged[2]
(a) Maleic	12.5	Good	Good
(b) PMDA[3]	12.3	Fair	Fair
(c) Diglycolic	13.4	Good	Good

1 Based on stability and turbidity measurements.
2 ASA/emulsifier mixture aged at 80°C for 3 hours.
3 Pyromellitic dianhydride, half mole/mole was used.

These results show that various cyclic anhydrides can be used to make emulsifiers of the present invention. The fact that emulsifier performance was the same after aging shows that the Igepal CO-630 was successfully capped in each case.

Example 5

Succinic anhydride was used to cap various polyethyleneoxy-containing surfactants as was done in Example 2 and the reaction products were tested as emulsifiers for ASA using the procedures described in Example 1. The results are listed in Table II. In Table II, the expression "EO" represents ethylene oxide units and the expression "PEG" represents polyethylene glycol. The ASA/emulsifier mixtures were aged at 80°C for 3 hours.

TABLE II

Emulsifiers Made by Capping Various Surfactants with Succinic Anhydride

Surfactant	Product HLB	ASA Emulsion Rating Fresh	ASA Emulsion Rating Aged
Alkyl Phenol Ethoxylates			
(a) C_8-$EO_{7.5}$	11.8	Fair	Fair
(b) C_8-$EO_{9.5}$	12.8	Good	Good
(c) C_8-$EO_{12.5}$	13.9	Good	Good
(d) C_9-EO_4	8.9	Ineffective	Ineffective
(e) C_9-EO_8	11.8	Good	Good
(f) C_9-$EO_{10.5}$	13.0	Good	Good
(g) C_9-EO_{12}	13.5	Excellent	Excellent
(h) C_9-EO_{100}	18.8	Not soluble at room temperature	Not soluble at room temperature
Alcohol Ethoxylates			
(i) Tergitol TMN-6	11.2	Poor	Poor
(j) Tergitol 15-S-9	12.7	Good	Good
(k) Tergitol 15-S-12	13.8	Good	Good
Fatty Acid Ethoxylates			
(l) PEG 300 Laurate	11.2	Poor	Poor
(m) PEG 400 Oleate	11.2	Fair	Fair
Miscellaneous			
(n) Ethoxylated sorbitan monostearate - EO_{20}	14.6	Good	Good
(o) Stearyl Amine - EO_{15}	13.3	Good	Good
(p) Pentaerythritol monolaurate	8.7	Very Poor	Very Poor
(q) Lauric Amide-EO_5	10.2	Ineffective	Ineffective

The results shown in Table II demonstrate that a variety of polyethyleneoxy-containing surfactants may be capped to form emulsifiers of the present invention. In each case, the capped emulsifier is stable when aged in mixture with ASA, giving the same emulsion power before and after aging. The results also show that, to be an effective emulsifier, the HLB of the capped emulsifier should lie between about 9 and 18. Below about 9, the capped emulsifier is ineffective. Above about 18, the emulsifier is not soluble in ASA.

Example 6

The emulsifier of Example 2 was mixed at the 10% level in several different types of ASA, namely:

(a) Straight chain C_{15-20} alkenyl ASA
(b) Isooctadecenyl ASA
(c) Isooctadecyl ASA
(d) A C_{20} ASA derived from a dimer of C_{10} straight chain alpha olefin.

(e) A branched chain ASA derived from tetrapropylene.

In each case, when tested by the procedures of Example 1, a stable emulsion was formed from both the freshly mixed and aged ASA/emulsifier mixtures.

Example 7

The capped emulsifier of Example 4(a) was isomerized using the procedure of U.S. Patent No. 3,953,616, Example 3. This converted the capping group from a maleyl group to a fumaryl group. Several changes were observed in the infrared spectrum, including a slight shift in the carbonyl to 1725 cm^{-1}, the appearance of trans olefin at 975 cm^{-1}, and the appearance of a band at 780 cm^{-1}.

This product, when tested by the procedures of Example 1, produced a stable ASA emulsion, both before and after aging the ASA/emulsifier mixture.

Example 8

The emulsifier product of Example 2 was used in a paper sizing experiment. The sizing agent was the ASA described in Example 6(a). Eight percent of the emulsifier was dissolved in the ASA and the mixture was held for about one month. Normal TAPPI (Technical Association of the Pulp and Paper Industry) laboratory handsheet procedures were followed using a 50/50 mixture of hardwood/softwood pulp, 0.4% ASA, and 1% cationic starch. A paddle stirrer was used to make the ASA/water emulsion. The handsheets were cured at 105°C for one hour. The sizing results, measured on a Hercules Size Tester, were equal to that obtained from the same ASA to which 7% Igepal CO-630 had been added just before emulsification.

CLAIMS

1. An emulsifier of the general formula:

$$R\text{–}W\text{–}[\text{–}Y\text{–}(COOH)_m]_n$$

wherein R is a hydrophobic alkyl, alkylaryl, arylalkyl or acyl group containing from 8 to 30 carbon atoms;

W is a water-soluble polyethyleneoxy-containing group having from 3 to 80 ethylene oxide units which is independently connected to R and Y through oxygen, sulfur, or nitrogen linkages;

$-[-Y-(COOH)_m]_n$ is a capping group for the oxygen, sulfur or nitrogen linkages on W not connected to R, wherein Y contains from 1 to 9 carbon atoms, provided that no more than 7 carbon atoms are methylene carbons;

m is 1 or 2;

n is 1/3, 1/2, 1, 2, or 3.

and the hydrophile-lipophile balance is between 9 and 18 on the HLB scale.

2. An emulsifier as claimed in Claim 1, wherein W has from 5 to 40 ethylene oxide units.

3. An emulsifier as claimed in Claim 1 or 2, wherein W is connected to R and Y through oxygen linkages.

4. An emulsifier as claimed in Claim 1, 2 or 3, wherein Y contains from 1 to 4 carbon atoms.

5. An emulsifier as claimed in Claim 1, 2, 3 or 4, wherein R–W– is derived from a hydroxyl-containing compound selected from:

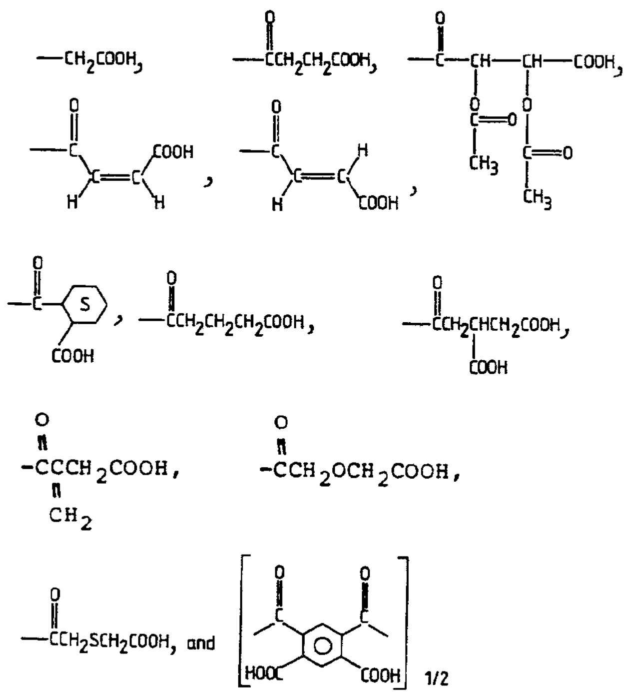
$$C_xH_{2x+1}-\overset{O}{\overset{\|}{C}}-(OCH_2CH_2)_z-OH,$$

$$C_xH_{2x+1}-C_6H_4-(OCH_2CH_2)_z-OH, \quad \text{and}$$

$$C_xH_{2x+1}-(OCH_2CH_2)_z-OH,$$

wherein x is an integer in the range from 8 to 24 and z is an integer in the range from 5 to 20.

6. An emulsifier as claimed in any preceding claim, wherein $[-Y-(COOH)_m]_n$ is selected from:



7. An emulsifier as claimed in any preceding claim, wherein the hydrophile-lipophile balance is from 11 to 16 on the HLB scale.

8. An emulsifier in accordance with Claim 1, substantially as described in any one of the foregoing Examples 2, 4, 5 and 7.

9. A stable hydrocarbyl-substituted succinic anhydride/emulsifier composition comprising:

(A) 70 to 99.5% of a normally liquid hydrocarbyl-substituted succinic anhydride containing from 6 to 50 carbon atoms in the substituent; and

(B) 0.5 to 30% of an emulsifier as claimed in any one of Claims 1 to 7.

10. A composition as claimed in Claim 9, wherein the hydrocarbyl substituent of component (A) is selected from alkyl, alkenyl and aralkyl.

11. A composition as claimed in Claim 9 or 10, wherein the hydrocarbyl substituent of component (A) contains from 10 to 30 carbon atoms.

12. A composition as claimed in Claim 9, 10 or 11, wherein the composition is in the form of an aqueous emulsion.

13. A stable succinic anhydride/emulsifier composition in accordance with Claim 9, substantially as described in any one of the foregoing Examples 3, 4, 5, 6 and 7.

14. A method of imparting water repellency to a surface containing groups reactive to anhydrides, which comprises impregnating said surface with an aqueous emulsion of a succinic anhydride/emulsifer composition as claimed in Claim 12.

15. A method according to Claim 14, wherein said surface is a cellulosic material.

16. A method of sizing paper which comprises the step of untimately dispersing within the wet pulp, prior to the ultimate conversion of said pulp into a dry web, an aqueous emulsion of a succinic anhydride/emulsifier composition as claimed in Claim 12.

17. A method of sizing paper in accordance with Claim 16, substantially as described in the foregoing Example 8.

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